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The Use of End-Loading Technique for the Sample Preparation of Organic Powders in X-Ray Powder Diffractometry

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Synopsis. The end-loading technique in preparing samples for X-ray powder diffractometry is found to be an effective method for reducing preferred orientation effects of organic powder samples.

In X-ray powder diffractometry, many attempts have been made to reduce the preferred orientation of mineral powders.[1-5] The end-loading technique has been found to be a simple and effective method for preparing the powder samples.[1] In this paper we report that the end-loading technique is very useful for reducing preferred orientations of organic powders. The powder samples examined in this study are those of benzamide,[6] benzoic acid,[7] α-form of pyrazinecarboxamide (PCA),[8] A-form of DL-2-aminobutyric acid (DL-ABA)[9] and DL-norleucine (DL-NL),[10] in which the latter two samples show marked tendency to orient on the 001 preferred orientation plane. In these samples, a quantitative examination of the preferred orientations in benzamide and PCA powders prepared by the normal (back-loading) technique have been made by Nakata et al.[11] Therefore, it is very interesting to compare the preferred orientations occurring in powders prepared by the normal and the end-loading techniques.

Experimental

The samples used in this study were ground by hand in an agate mortar. The specimen holder was constructed from a usual aluminum-holder by cutting away the end piece, by cementing a ground glass-slide onto the back and by covering the top surface with a glass-slide (see Fig. 2 of Niskanen[1]). The powder sample was then poured and packed in the holder by tapping it at the bottom.

All diffraction patterns taken by the normal and the end-loading techniques were obtained using a Rigaku Geigerflex (CN2013). The experimental conditions were: Cu $K\alpha$ radiation, a nickel filter, 0.5° divergence and 0.15 mm receiving slits, a scintillation detector and a scan speed of $1/2°(2\theta\,\mathrm{min}^{-1})$. Intensity measurements of the diffraction peaks were made by cutting out background-subtracted peak areas from each of the traces and weighing.

Results and Discussion

The degree of randomness of oriented powder particles is given by[11]

$$R_0 = \frac{\Sigma|I_{\mathrm{obs}}-I_{\mathrm{ran}}|}{\Sigma|I_{\mathrm{ran}}|} \tag{1}$$

where I_{obs}'s are the observed intensities and I_{ran}'s, which are calculated from F_o's obtained by single-crystal work, are the intensities from a sample with completely random orientation.

In order to assess the effect of the end-loading technique on the reduction of preferred orientation, we took two diffraction patterns from the same grounded powder using the normal and the end-loading techniques. Table 1 lists the R_0 values for the

Table 1. R_0 Values and Preferred Orientation Parameters in the Powder Samples Prepared by the Normal and the End-Loading Techniques

Sample		R_0	Plane or axis		Orientation parameter					Relative volume			$\mu^{d)}/\mathrm{cm}^{-1}$
			1	2	C_0	C_1	P_1	C_2	P_2	V_0	V_1	V_2	
Benzamide	Normal	0.44	(001)	$(\bar{1}04)$	0.02	0.70	6	0.28	5	0.09	0.61	0.30	7.2
	End-	0.20	(100)	$(\bar{1}04)$	0.44	0.29	10	0.27	17	0.86	0.09	0.05	
Benzoic acid	Normal	0.43	b-axis	(001)	0.22	0.49	19	0.29	11	0.55	0.35	0.10	8.1
	End-	0.22	(100)	$(\bar{1}02)$	0.40	0.46	23	0.14	8	0.87	0.08	0.05	
PCA[a)]	Normal	0.47	c-axis	(100)	0.06	0.28	3	0.66	4	0.16	0.42	0.42	9.1
	End-	0.15	(110)	(001)	0.29	0.40	1	0.31	29	0.59	0.37	0.04	
DL-ABA[b)]	Normal	1.14	(001)	—	0.01	0.99	35	—	—	0.05	0.95	—	8.2
	End-	0.19	(110)	(100)	0.50	0.37	10	0.13	5	0.85	0.09	0.06	
DL-NL[c)]	Normal	0.74	(001)	—	0.01	0.99	27	—	—	0.10	0.90	—	7.2
	End-	0.28	(210)	$(\bar{1}11)$	0.16	0.58	11	0.26	63	0.64	0.32	0.04	
Gypsum	Normal	0.81	(010)	(011)	0.00	0.94	31	0.06	50	0.05	0.91	0.04	140
	End-	0.71	(010)	(011)	0.00	0.91	25	0.09	22	0.03	0.88	0.09	
Olivine	Normal	0.36	(010)	(001)	0.02	0.82	10	0.16	15	0.11	0.77	0.12	386
	End-	0.25	(010)	(001)	0.05	0.66	11	0.29	17	0.29	0.54	0.17	

a) α-form of pyrazinecarboxamide. b) A-form of DL-2-aminobutyric acid. c) DL-norleucine. d) Linear absorption coefficients for Cu$K\alpha$ radiation.

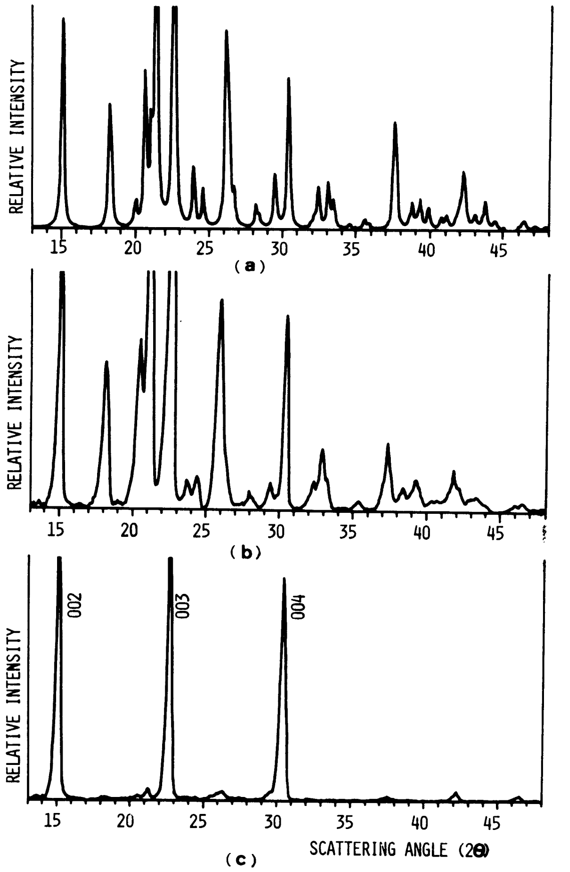

Fig. 1. The observed and calculated diffraction patterns of DL-ABA. a) An "ideal" pattern calculated from I_{ran}.⁹⁾ b) The observed pattern taken by the end-loading technique. c) The observed pattern taken by the normal technique.

powder samples of benzamide,⁶⁾ benzoic acid⁷⁾ and PCA⁸⁾ obtained by the two different techniques. Comparing R_0 values in Table 1, it is seen that the end-loading technique effectively reduces the R_0 values to under one-half of the values of the normal technique.

Further, we examined the usefulness of the end-loading technique using the samples of DL-ABA⁹⁾ and DL-NL.¹⁰⁾ These powder particles have a habit of thin plate with well developed (001) faces. It therefore show a marked tendency to orient on the 001 preferred orientation plane. Figure 1 shows the observed diffraction patterns of DL-ABA taken by the normal and the end-loading techniques. For comparison, an "ideal" pattern calculated from I_{ran}⁹⁾ of DL-ABA¹²⁾ is also shown in Fig. 1(a).

As can be seen in Fig. 1, the observed pattern taken by the normal technique yields only the 00*l* diffraction peaks, whereas the pattern taken by the end-loading technique is in good agreement with the "ideal" pattern. The R_0 values obtained by the normal and the end-loading techniques are 1.14 and 0.19, respectively (Table 1). Similarly, a marked decrease of the R_0 value can also be seen in the case of DL-NL; the R_0 values for the powder samples prepared by the normal and the end-loading techniques are 0.74 and 0.28, respectively.

Here, we examine quantitatively the above reduction of preferred orientations using the method of Nakata et al.¹¹⁾ Table 1 lists the preferred orientation parameters, C_i and P_i, for the powders prepared by the normal and the end-loading techniques. The relative volumes of the domains, V_i, in the powder are also listed in Table 1, where a domain is defined as a collection of particles having the same preferred orientation plane or axis.¹¹⁾ Comparing V_i values, one can see that the V_0 values of the end-loading technique are much larger than those of the normal technique, indicating that the randomly oriented domains are effectively increased in volume by the use of the end-loading technique. Further it is interesting that most of the preferred orientation planes or axes observed in the powders prepared by the normal technique disappear, and the different planes or axes with small relative volumes appear in the powders prepared by the end-loading technique.

The drastic reduction of preferred orientation effects described above may be explained as follows: Since the end-loading technique applies no pressure normal to the surface of the specimen, the powder particles except for those very near to the surface are not effected by the glass-slide. Furthermore, since organic substances generally have small absorption coefficients for X-rays (Table 1), the organic powder in a holder may allow considerable penetration of the X-ray beam. From the above results, the degree of preferred orientation of powder particles is estimated to be much lower than that of the normal technique.

In order to clarify the effect of absorption, we applied the normal and the end-loading techniques to inorganic powder samples gypsum¹³⁾ and olivine¹⁴⁾; these samples have large absorption coefficients (see Table 1). The preferred orientation parameters, C_i and P_i, and the relative volumes of the domains, V_i, in these powders are listed in Table 1. As expected, no marked decrease in R_0 (and increase in V_0) can be seen in the powders prepared by the end-loading technique. In addition, the same preferred orientation plane or axis is found in both the powders prepared by the two techniques, and that the differences in V_i are rather small.

Consequently, we may say that the end-loading technique effectively minimizes the preferred orientations of organic powder samples, especially for those with low absorption coefficients.

References

1) E. Niskanen, *Am. Mineral.*, **49**, 705 (1964).
2) A. M. Bystrom-Asklund, *Am. Mineral.*, **51**, 1233 (1966).
3) F. D. Bloss, *Am. Mineral.*, **52**, 1243 (1967).
4) R. Hughes and B. Bohor, *Am. Mineral.*, **55**, 1780 (1970).
5) S. T. Smith, R. L. Snyder and W. E. Brownell, *Adv. X-Ray Anal.*, **22**, 77 (1978).
6) C. C. F. Blake and R. W. H. Small, *Acta Crystallogr., Sect. B*, **28**, 2201 (1972).
7) G. Bruno and L. Randaccio, *Acta Crystallogr., Sect. B*, **36**, 1711 (1980).

8) Y. Takaki, Y. Sasada, and T. Watanabè, *Acta Crystallogr.*, **13**, 693 (1960).

9) K. Nakata, Y. Takaki and K. Sakurai, *Mem. Osaka Kyoiku University, Ser. III,* **28**, 73 (1980).

10) A. M. Mathieson, *Acta Crystallogr.*, **6**, 399 (1953).

11) K. Nakata, H. Sugihara, S. Mori, H. Yamaguchi, and Y. Takaki, *Bull. Chem. Soc. Jpn.*, **57**, 3395 (1984).

12) The relative intensity tables (I_{obs} and I_{ran}) of benzamide, benzoic acid, PCA, DL-ABA and DL-NL are kept at the Office of the Chemical Society of Japan (Document No. 8722).

13) W. F. Cole and C. J. Lancucki, *Acta Crstallogr., Sect. B,* **30**, 921 (1974).

14) H. Yamaguchi, K. Akatsuka, A. Kurisu, Y. Takaki, and M. Setoguchi, Annual Meeting of Mineralogical Society of Japan, Tsukuba, June 1982, Abstr., No. 36.